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On the analysis of derivative thermoluminescence and derivative differential thermal analysis curves

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Abstract : We present a method of determination of trapping parameters by using derivative thermoluminescence (DTL) curves. The method is applied both to numerically computed and experimental thermoluminescence (TL) peaks. Finally, the method is extended to analyse differential thermal analysis (DTA) curves.

Keywords : Derivative thermoluminescence curve (DTL), derivative differential thermal analysis (DDTA) curve, trapping parameters

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1. Introduction

Measurements of thermoluminescence (TL) glow curves have been found to be useful for the determination of crystal trapping parameters which is an important area of research in condensed matter physics dealing almost equally with microscopic and macroscopic systems [1]. The different methods for the evaluation of these parameters namely activation

energy (E), order of kinetics (b) and pre-exponential factor (s) have been recently reviewed [2,3]. The further importance of the analysis of TL curves emanates from their wide applications in archeology and dosimetry [4,5]. In the present paper we consider a method of the determination of trapping parameters by using the derivative TL (DTL) curves. The advent of modern instrumentation techniques, primarily the ease and flexibility of instrument control by microprocessor have made automatic data control and processing a reality. As a result the experimental difficulties associated with the analysis of DTL curves can be surmounted. In the following sections we describe the numerical computation of DTL curves, their characteristics and present equations for the calculation of trapping parameters from DTL curves. We apply the present method both to numerically generated and experimental peaks.

Finally we extend the method developed to analyse curves of differential thermal analysis [5,6] (DTA), which has found wide applications in a number of areas such as the analysis of different phase transitions and in kinetic studies [7–9].

2. Computation of DTL curves

2.1. Theory :

The equations for first order ($b = 1$) and general order ($b \neq 1$) TL peaks can be written as [3]

$$\frac{I}{I_m} = \exp\left[u_m - u + F(u, u_m)\right] \quad (b = 1) \tag{1}$$

and

$$\frac{I}{I_m} = \exp\left(u_m - u\right)\left[1 - \frac{(b-1)}{b} F(u, u_m)\right]^{-\frac{b}{(b-1)}} \quad (b \neq 1) \tag{2}$$

with

$$F(u, u_m) = u_m^2 \exp\left(u_m\right)\left[\frac{E_2(u_m)}{u_m} - \frac{E_2(u)}{u}\right], \tag{3}$$

where b is the order of kinetics, I is the TL intensity at any temperature T, I_m is the intensity at peak temperature T_m, $u = E/kT$ and $u_m = E/kT_m$, k being the Boltzmann constant. $E_2(u)$ is the second exponential integral [10].

From eqs. (1) and (2)

$$\frac{dI}{dT} = -\frac{ku^2}{E}\frac{dI}{du} \tag{4}$$

with

$$\frac{dI}{du} = I\left(\frac{dF}{du} - 1\right) \text{ for } b = 1 \tag{5}$$

and

$$\frac{dI}{du} = -I + \frac{dG}{du} \exp\left(u_m - u\right) \text{ for } b \neq 1, \tag{6}$$

where

$$G = D^{-\frac{b}{(b-1)}} \tag{7}$$

and

$$D = 1 - \frac{(b-1)}{b} F(u, u_m). \tag{8}$$

Eq. (4) can be differentiated to give

$$\frac{d^2I}{dT^2} \quad \frac{k^2u^3}{E^2}\left[2\frac{dI}{du} + u\frac{d^2I}{du^2}\right], \tag{9}$$

where $$\frac{d^2I}{du^2} = \frac{dI}{du}\left(\frac{dF}{du} - 1\right) + I\frac{d^2F}{du^2} \quad (b = 1) \tag{10}$$

and $$\frac{d^2I}{du^2} = -2\frac{dI}{du} - I + \frac{d^2G}{du^2}\exp(u_m - u) \quad (b \neq 1). \tag{11}$$

2.2. *Definition of derivative thermoluminescence (DTL) curves :*

The curve of thermoluminescence intensity I against temperature T is called a TL curve. Here, the curve of dI/dT against T is the first DTL curve and the curve of d^2I/dT^2 *versus* T is the second DTL curve. So one can compute TL curves by using eqs. (1) and (2), whereas first DTL curve can be simulated by employing eqs. (4)–(6). Again eqs. (9)–(11) lead to the computation of second DTL curve.

3. Characteristics of DTL curves

3.1. *Characterization of DTL curves :*

TL, first DTL and second DTL curves for $b = 1$ and $b = 2$ are respectively shown in Figures 1 and 2. It is seen from these figures that on differentiation, the single peak of TL

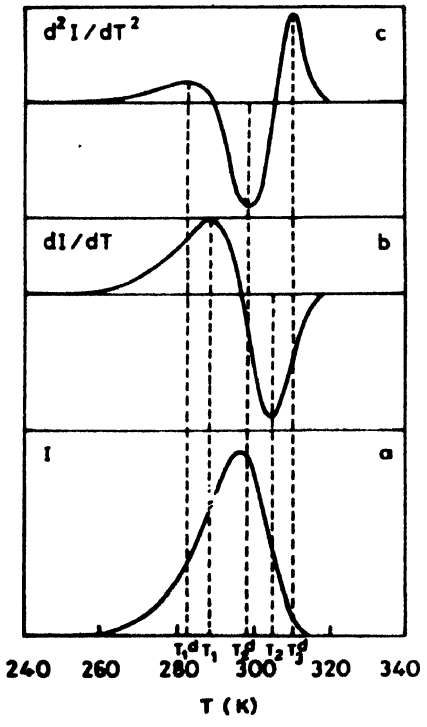

Figure 1. Computer generated DTL curves : $b = 1$, $s = 10^{13}$ sec^{-1}, $E = 0.8854$ eV, $\beta = 0.1667$ K sec^{-1} : (a) TL curve, (b) First DTL curve, (c) Second DTL

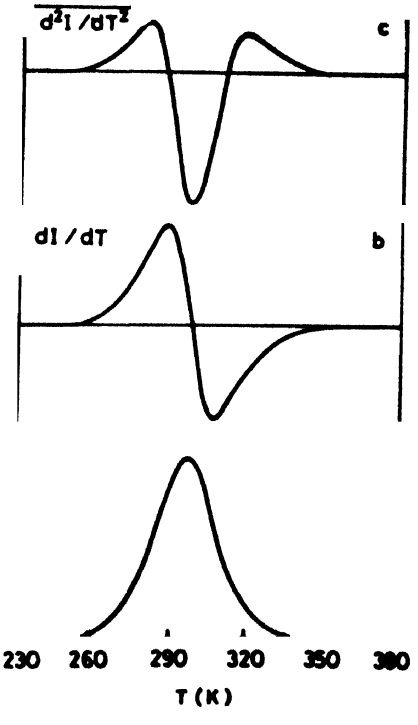

Figure 2. Same as in Figure 1 but for $b = 2$.

curve, is converted into one maximum and a minimum in the first DTL curve; while there are two maxima and a minimum in the second DTL curve. For first order DTL (Figure 1), the absolute value of the maximum is smaller than that of the minimum in the first DTL curve; and the absolute value of the first maximum is smaller than that of the second maximum in the second DTL curve. For second order TL (Figure 2), the shapes are markedly different; the absolute values of the maximum and the minimum are approximately the same in the first DTL curve, and in the second DTL curve, a pair of symmetrical maxima is observed. Therefore, the characteristics of DTL curves can indicate the order of kinetics.

3.2. *Separation of overlapping peaks :*

It is well known that it is not straightforward to distinguish overlapping peaks corresponding to two kinds of traps in the TL curve. However, it is obvious in the first DTL curve that there are two maxima (at 267 and 288 K) and two minima (at 280 and 304 K).

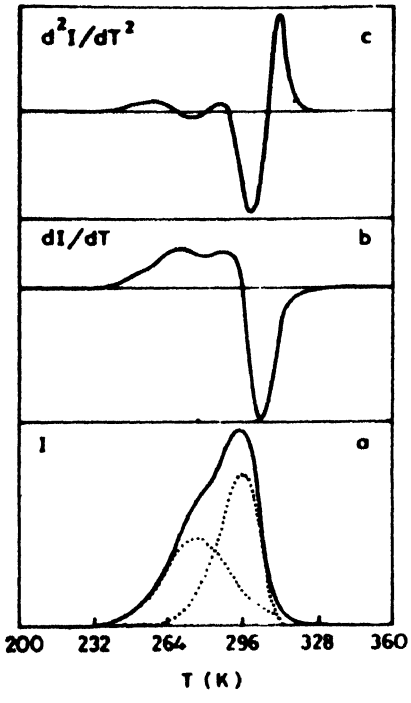

Figure 3. Computer simulated DTL curves of overlapping peaks. First peak : $b = 1$, $s = 10^{13}$ sec^{-1}, $E = 0.8854$ eV, $\beta = 0.1667$ K sec^{-1}, Second peak : $b = 2$, $s = 10^{10}$ sec^{-1}, $E = 0.6707$ eV, $\beta = 0.1667$ K sec^{-1}, (a) TL curve, (b) First DTL curve, (c) Second DTL curve.

Because each individual trapping state would have one maximum and one minimum in the first DTL curve, the first DTL curve with two maxima and two minima indicates the existence of two traps. The second DTL curve shows three maxima (at 257, 284 and 309 K) and two minima (at 275 and 299 K). Because each individual trap would have two maxima

and one minimum in the second DTL curve, from the second DTL curve with three maxima and two minima, one can conclude the presence of two traps. Therefore, both the first and second DTL curves reveal the presence two distinct peaks corresponding to different traps in the TL peak profile in Figure 3. Hence DTL curves can indicate the presence of overlapping peaks.

4. Determination of trapping parameters

Let T_1 and T_2 ($T_2 > T_1$) be the temperatures corresponding to the maximum and minimum in the first DTL curve. It is found that to a very good approximation a linear relation exists between u_1 and $u_1/(u_1 - u_2)$ where $u_1 = \frac{E}{kT_1}$ and $u_2 = \frac{E}{kT_2}$ so that

$$u_1 = A\frac{u_1}{u_1 - u_2} + B \tag{12}$$

which leads to

$$E = Ak\frac{T_1T_2}{(T_2 - T_1)} + BkT_1. \tag{13}$$

The coefficients A and B have been evaluated by using the technique of linear regression [11] in which the maximum of the absolute value of the fractional error in u_1 is minimized. The coefficients A and B depend on the order of kinetics. In Table 1, the coefficients A and B have been tabulated for some values of the order of kinetics.

Table 1. Coefficients C and D occurring in equation (13) for the determination of the activation energy from the first DTL curve.

Relation between	b	C	D
	1.0	−0.5965	1.9246
	1.5	−1.2911	2.3168
T_1, T_2	2.0	−1.9172	2.6317
	2.5	−2.4870	2.8968
	3.0	−3.0092	3.1263

Similarly, let T_{d1} and T_{d3} be the temperatures corresponding to two maxima and T_{d2} be the temperature corresponding to the minimum in the second DTL curve ($T_{d1} < T_{d2} < T_{d3}$). In this case, also a plot of $u_{di}\left(= \frac{E}{kT_{d_i}}\right)$ against $u_{di}/(u_{di} - u_{dj})$ $\left(\text{where } u_{dj} = \frac{E}{kT_{dj}}\right)$ with $T_{di} < T_{dj}$ is found to be linear enabling us to write

$$u_{di} = C\frac{u_{di}}{(u_{di} - u_{dj})} + D, \tag{14}$$

so that

$$E = Ck\frac{T_{di}T_{dj}}{(T_{dj} - T_{di})} + DkT_{di}. \tag{15}$$

Again the coefficients C and D have been evaluated by using the technique of linear regression [11]. C and D depend on the order of kinetics and have been tabulated in Table 2 for different values of b.

Table 2. Same as Table 1 but for second DTL curve [cf. eq. (15)].

Relation between	b	C	D
	1.0	0.3229	2.0895
	1.5	0.7612	2.0784
T_{d1}, T_{d2}	2.0	0.3189	2.2892
	2.5	–0.0355	2.4636
	3.0	–0.3567	2 6110
	1.0	–0.1050	3.2969
	1.5	–2.9760	1.9431
T_{d2}, T_{d3}	2.0	–4.0719	2.2881
	2.5	–4.9105	2.5714
	3.0	–6.5893	2.9399
	1.0	–0.7905	1.2067
	1.5	–1.0464	4 0170
T_{d1}, T_{d3}	2.0	–1.8670	4.5769
	2.5	–2.5341	5.0354
	3.0	–3.6182	5.5487

In the present paper we suggest a method of determination of order of kinetics based on the work of Kissinger [12] for different thermal analysis. For TL, the Kissinger shape index K can be expressed as

$$K = \left| \frac{\left(\frac{dI}{dT}\right)_{T=T_1}}{\left(\frac{dI}{dT}\right)_{T=T_2}} \right|. \tag{16}$$

K is the ratio of the magnitudes of the absolute values of the maximum and the minimum in the first DTL curve and like the symmetry factor μ_g introduced by Chen [13,14], K can also indicate the order of kinetics of a TL peak.

Knowing E and b the pre-exponential factor s can be evaluated from the following eqs. [3]

$$s = \frac{\beta k}{E} u_m^2 \exp(u_m) \quad (b = 1), \tag{17}$$

$$s = \frac{\beta k u_m^2 \exp(u_m)}{E[b - (b-1)u_m \exp(u_m) E_2(u_m)]} \quad (b \neq 1) \tag{18}$$

5. Results and discussions

The computation of TL, first and second DTL curves requires the evaluation of the second exponential integral $E_2(u)$. We use the computer code developed by Devi [15] to evaluate $E_2(u)$ by expressing it in terms of continued fraction. The temperatures T_1 and T_2 of first DTL curve have been obtained by solving the equations

$$\frac{d^2I}{dT^2} = \frac{k^2u^3}{E^3}\left[2\frac{dI}{du} + u\frac{d^2I}{du^2}\right] = 0 \tag{19}$$

numerically by Newton-McAuley method [16]. Again the temperatures T_{d1}, T_{d2} and T_{d3} of the second DTL curve have been computed numerically from the equation

$$\frac{d^3I}{dT^3} \quad \frac{k^3u^4}{E^3}\left[u^2\frac{d^3I}{du^3} + 6u\frac{d^2I}{du^2} + 6\frac{dI}{du}\right] = 0 \tag{20}$$

The solution of eq. (20) presents some problems for the computation of T_{d2} and T_{d3}. This diffuculty has been overcome in some cases by using bisection method [16] in conjunction with McAuley method as done by Singh *et al* [17] in the case of differential thermal analysis curves. Following Singh *et al* [17], we have also directly computed first and second DTL curves from TL curves by using the qubic spline method [16] and hence obtained the temperatures T_1, T_2, T_{d1}, T_{d2} and T_{d3}. The values of T_i $(i = 1, 2)$, T_{di} $(i = 1, 2, 3)$ so obtained are in excellent agreement with those obtained by solving eqs. (19) and (20).

The Kissinger shape index parameter K depends not only on the order of kinetics but also on $u_m = \frac{E}{kT_m}$. In Figure 4, we show the variation of K with u_m for a number of values

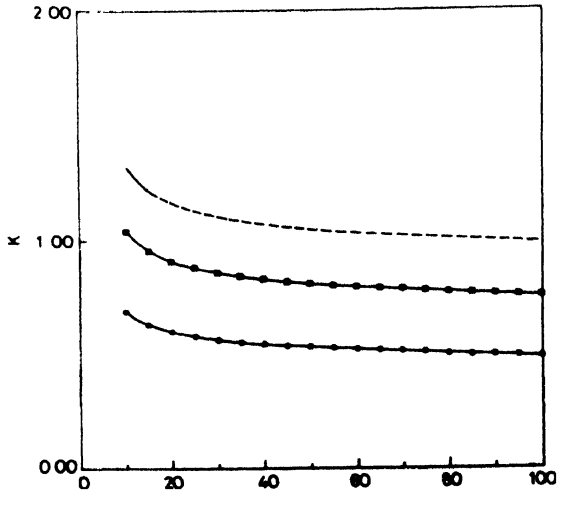

Figure 4. Variation of Kissinger shape index K with u_m for $b = 1$ (•
$b = 1.5$ (■–■–■–■) and $b = 2.0$ (– – – –)

of b namely $b = 1$, 1.5 and 2. It is evident from Figure 4 that beyond $u_m > 20$ K is almost independent of u_m. For most of the observed TL peaks $20 \leq u_m \leq 40$. As a result we have

calculated average K for $20 \leq u_m \leq 40$ for each value of b between $1 \leq b \leq 3$. Finally, the average K has been expressed as a quadratic function of b ($1 \leq b \leq 3$) using the standard technique of non-linear regression [18] for $1 \leq b \leq 3$ enabling us to write

$$K = -0.07273 + 0.7275\, b - 0.06419\, b^2. \tag{21}$$

As a check of the present method of the determination of trapping parameters, we apply it to number of numerically computed TL curves. In Table 3, we show the values of the trapping parameters E_c, s_c and b_c computed by the present method together with their input values E_{in}, s_{in} and b_{in}. A fair agreement between the input and the calculated values of trapping parameters is observed. It is to be noted that the calculated value of activation energy shown in Table 3 is actually the average of five values obtained by using the pairs of temperatures (T_1, T_2), (T_{d1}, T_{d2}), (T_{d2}, T_{d3}) and (T_{d3}, T_{d1}).

Table 3. Trapping parameters of some computer generated TL peaks as calculated by the present method.

E_{in} (eV)	s_{in} (sec^{-1})	b_{in}	E_c (eV)	s_c (sec^{-1})	b_c
0.8859	1.0×10^{13}	1.0	0.8864	$1\,002 \times 10^{13}$	0.968
0.8859	1.0×10^{13}	1.5	0.8862	1.013×10^{13}	1 474
0.8859	1.0×10^{13}	2.0	0.8864	1.022×10^{13}	1.952
0.8859	1.0×10^{13}	2.5	0.8865	$1\,028 \times 10^{13}$	2.432
0.8859	1.0×10^{13}	3.0	0.8869	1.043×10^{13}	2 941

Finally, we consider the applicability of the present method to the 200°C experimental TL peak of NaCl : I irradiated with 2.04 KGy of γ-rays and record with a linear heating rate of $\beta = 1.5°C\, s^{-1}$ [19]. Again we obtain fair agreement between the

Table 4. Trapping parameters of experimental 200°C TL peak of NaCl : I irradiated with 2.04 kGy of γ-rays recorded with $\beta = 1.5°C\ sec^{-1}$ [19].

E_{cf} (eV)	s_{cf} (sec^{-1})	b_{cf}	E_c (eV)	s_c (sec^{-1})	b_c
1.145	2.0×10^{11}	1.5	1.150	1.566×10^{11}	1.504

trapping parameters (E_c, s_c and b_c) calculated by the present method and those (E_{in}, s_{in} and b_{in}) obtained by Singh *et al* [19] using the rigorous method of curve fitting [20].

6. Analysis of differential thermal analysis curves

The present method finds straight forward applications to differential thermal analysis (DTA) curves. Following Singh *et al* [17], one can write for first order ($b = 1$) and non-first order ($b \neq 1$) DTA curves

$$\frac{\Delta T}{(\Delta T_m)_m} = \exp\left[u_m - u + F(u, u_m)\right] \quad (b = 1) \tag{22}$$

and $$\frac{\Delta T}{(\Delta T_m)_m} = \exp(u_m - u)\left[1 - \frac{b-1}{b} F(u, u_m)\right]^{\frac{b}{b-1}} \quad (b \neq 1) \tag{23}$$

with $$F(u, u_m) = u_m^2 \exp(u_m)\left[\frac{E_2(u_m)}{u_m} - \frac{E_2(u)}{u}\right], \tag{24}$$

where ΔT is the temperature deviation from the base line at temperature T and $(\Delta T)_m$ is the maximum value of ΔT. $u = \frac{E}{kT}$ and $u_m = \frac{E}{RT_m}$, T_m is the peak temperature, R is the

Table 5. Kinetic parameters from the experimental DTA peak corresponding to the process $[Ni(mpipz)_2(NCS)_2].2H_2O \rightarrow Ni(mpipz)_2(NCS)_2$

E_{cf}(KJ)	s_{cf}(sec^{-1})	b_{cf}	E_c (KJ)	s_c (sec^{-1})	b_c
143.90	7.83×10^{16}	1.5	143.94	7.93×10^{16}	1.448

universal gas constant. It is clear that eqs. (22–24) closely resemble eqs. (1–3) for TL curves. So the foregoing analysis for the determination of trapping parameters of TL curves can be directly applied to the computation of kinetic parameters of DTA curves. The equations for the first and second derivative differential thermal analysis curves (DDTA) can be computed respectively from the equations

$$\frac{d(\Delta T)}{dT} = -\frac{Ru^2 d}{E}\frac{d(\Delta T)}{du} \tag{25}$$

and $$\frac{d^2(\Delta T)}{dT^2} = \frac{R^2 u^3}{E^2}\left[2\frac{d(\Delta T)}{du} + u\frac{d^2(\Delta T)}{du^2}\right]. \tag{26}$$

On comparing eqs. (25) and (26) with eqs. (4) and (9) respectively, we find that eqs. (13) and (15) can also be used to compute the activation energy of DTA peaks and if we replace k by R, the eq. (21) connecting the Kissinger shape index K and b can be used for the evaluation of order of kinetics (b). Knowing b and E, one can determine the pre-exponential factor from eqs. (17) and (18).

We apply the present method to compute the kinetic parameters of the DTA curve [21,22] of the dehydration of $Ni[(mpipz)_2(NCS)_2]$ where mpipz stands for N-methylipiperazine. The above mentioned DTA curve has also been analysed by Devi [15] using a rigorous computer code of curve fitting. Here also, we find a resonable agreement between the values of kinetic parameters.

7. Conclusion

In the present paper we develope a method of evaluation of trapping parameters from TL peak by using the first and second derivative TL (DTL) curves. The suitability of the present method is judged by applying it to extract trapping parameters of computer simulated and experimental TL peaks. It is also shown that the method can also be used to determine kinetic parameters from a DTA curve.

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